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PRODUCTION OF POLYESTER
[Poriesuteru no Seizohoho]

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1. Title of the Invention

Production of Polyester

2. Scope of the Claims

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A method of producing polyesters characterized in that when producing polyesters by reacting a bifunctional carboxylic acid primarily consisting of terephthalic acid as an acid component and its ester-forming derivative with a glycol primarily consisting of an ethylene glycol component or its ester-forming derivative, and subsequently polymerizing the reaction product to produce polyesters, antimony tetroxide is used as a polymerization catalyst.

3. Detailed Description of the Invention

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The present invention relates to a method of producing polyesters with excellent color and transparency that are suitable for producing fibers for clothing and industrial uses, films and molding materials.

Presently, polyesters that are manufactured industrially are produced by the following two-step reaction: a first stage reaction wherein a polyester, particularly polyethylene terephthalate is prepared by direct esterification of terephthalic acid or dimethyl terephthalate and ethylene glycol or an ester exchange reaction to obtain bis-(2-hydroxyl)terephthalate and/or its lower polymer, and a second stage reaction wherein the reaction product undergoes a polycondensation reaction under a high temperature leading to polyesters with high degrees of polymerization. The first stage

* Numbers in the margin indicate pagination in the foreign text.

reaction and the second stage reaction are carried out at a high temperature using a certain kind of catalyst in a certain form. In this case, there are tremendous differences in the quality of polyester polymers and the time required for production based on the kind and quantity of the catalysts used.

Conventionally, in the reaction of producing glycol ester at the first stage, organic acid metal salts or metal chelates such as zinc acetate, calcium acetate, barium acetate, manganese acetate, manganese formate, lead acetate, magnesium acetate and zinc acetylacetonate, and hydrides, alkoxides or hydroxides of lithium, sodium, calcium and magnesium, are added as a catalyst. However, the catalysts added when producing glycol esters are likely to generate clouding, which is assumed to be caused by coloring/discoloring of polymers and degeneration of catalysts due to the effects of impurities in the reaction system when carrying out the polymerization reaction at a high temperature under high vacuum levels in the second stage reaction, resulting in a significant reduction in the commercial values of the products obtained. Thus, prevention of these effects is considered to be very important from an industrial aspect.

Conventionally, for similar purposes, organic or inorganic phosphorus compounds such as phosphoric acid, phosphorous acid or triphenyl phosphite are added at the end of said first stage reaction. However, these additives are disadvantageous since they may lower the softening points of the polymers obtained or they may cause coloring in gray. In particular, even when using a

which is known as the best polymerization catalyst, [REDACTED] in [REDACTED] and this is a serious drawback in the cases of polyester fibers for clothing which require high quality products from the market. In particular, this trend [REDACTED] when the polycondensation reaction lasts for a long time (150 min. or longer) or [REDACTED]. This clouding is assumed to be attributed to the fact that the catalyst is degenerated. Besides the disadvantage in terms of reaction speed, this may become a cause for problems in the post-processes such as spinning defects during spinning due to a reduction in solubility in the system of inactivated catalyst.

For this reason, a method of adding an oxidant such as potassium permanganate to the latter half of the polymerization was proposed (see F.P1471776) and a method of adding a sulfur compound during polymerization was also proposed (Japanese Patent No. 42 [1967]-4995). Even with these methods, if the amount of trivalent antimony compound is high or if the reaction time extends, not only the effect of preventing coloration is exhibited, but also yellowing appears which seems to be due to decomposition of coloring inhibitor. Therefore, it was difficult to produce polyesters with high transparency and /162 satisfactory coloring as well as high degrees of polymerization.

The inventors earnestly investigated in an attempt to solve these problems and as a result it was discovered that when [REDACTED]

[REDACTED] especially antimony tetroxide as a polymerization catalyst during production of polyesters, [REDACTED]
[REDACTED]
[REDACTED] and a colorless transparent polyester was found to be produced with a high degree of polymerization. This finding led us to achieve the present invention.

Namely, the present invention provides a method of producing polyesters characterized in that, when producing polyesters by reacting a bifunctional carboxylic acid primarily consisting of terephthalic acid as an acid component and its ester-forming derivative with a glycol primarily consisting of an ethylene glycol component or its ester-forming derivative, and subsequently polymerizing the reaction product to produce polyesters, antimony tetroxide is used as a polymerization catalyst.

Polyesters described in the method of this invention are primarily targeted for polyethylene terephthalate. A mixture comprising terephthalic acid at 80 mol% or greater and one or more kinds of bifunctional acids such as isophthalic acid, phthalic acid, adipic acid, sebacic acid, *p*-hydroxybenzoic acid, *p*- β -hydroxybenzoic acid, ω -hydroxycaproic acid at 20 mol% or less can be used as an acid component. A mixture of ethylene glycol at 80 mol% or greater and one or more kinds of diol compounds such as trimethylene glycol, hexamethylene glycol, cyclohexanedimethanol(1,4), 2,2-4,4-tetramethylcyclobutanediol(2,4), hydroquinone at 20 mol% or less can be used as a glycol component.

The amount of antimony tetroxide to be added according to the method of this invention is not particularly limited. From the standpoint of solubility in the reaction system and the effective use of the catalyst, a range from [REDACTED] or less and particularly from [REDACTED] desirable relative to the entire acid component in the polyester.

In terms of timing of the addition of antimony tetroxide, it can be added at any time before the completion of the polycondensation reaction. However, it is most desirable to be added before the initial stage of the polycondensation reaction for the purpose of maintaining sufficient solubility in the reaction system and effectively using it in the polycondensation reaction. As a method of adding antimony tetroxide, the prior art and a variety of addition methods that have been used in practice can be employed directly. When considering the fact that the solubility of antimony tetroxide is less than that of antimony trioxide, it is particularly effective if it is dissolved in advance in ethylene glycol under pressure with heating.

According to the method of this invention, known additives that are used in the production of conventional polyesters such as phosphorous acid and triphenyl phosphate can be used. Furthermore, other known ester exchange catalysts and polymerization catalysts such as compounds containing metals including Li, Na, K, Cs, Ca, Mg, Be, Sr, Ba, Zn, Cd, B, Al, Pb, Mn, Fe, Co, Sb, Sn, Si, La, Nd, Ti, Zr, Ce and the like can be used, or the effects can be enhanced by using them

with a monomer. In particular, in the present invention, use of both antimony tetroxide and antimony trioxide accelerates the production of polyester with satisfactory whiteness.

According to the present invention, polyesters with a high degree of polymerization can be obtained very easily along with satisfactory color and transparency.

Next, the present invention will be explained with reference to the following embodiments. The limiting viscosity of the polymer as mentioned in the method of the present invention is measured by the following method. Orthochlorophenol polymer is dissolved at 100°C for a period of 90 min. and the limiting viscosity is determined at 35°C using an Oswald viscometer. With respect to the samples for measuring the degree of whiteness, samples are left standing at 140°C for 4 hours to be crystallized completely. The degree of whiteness is determined with a Hunter type colorimeter.

Embodiment 1

222 mol% of ethylene glycol and 0.1 mol% of calcium acetate monohydrate as a catalyst were added to dimethyl terephthalate to carry out an ester exchange reaction. A catalyst solution prepared by dissolving 0.03 mol% of antimony tetroxide in 20 mol% of ethylene glycol at 250°C under pressure was added. Moreover, 0.1 mol% phosphoric acid aqueous solution was added to carry out polymerization. The reaction was carried out while maintaining the mixture under atmospheric pressure for 30 minutes, subsequently under reduced pressure of 15 mmHg for 30 minutes and further under a reduced

pressure of 0.1 mmHg. The reaction temperature was slowly elevated to 277°C. The reaction mixture was sampled at 120 min. after starting /163 the reaction in high vacuum state, and limiting viscosity, the degree of whiteness and softening point were measured.

The results are shown in Table 1 (L, a, b in the table are values calculated using the Hunter colorimeter and represent the following values).

L: Reflective index in %

a: Green→Red: a higher value implies that redness is stronger.

b: Blue→Yellow: a higher value implies that yellowness is stronger.

Table 1

a 実験番号	b 触媒モル%	c 限粘度	d 化点	L	a	b
実施例 1 e	Sb ₂ O ₄ 0.03	0.64	260.0	78.0	-0.8	0.7
2	Sb ₂ O ₄ 0.03	0.60	259.5	75.0	-0.9	1.3
3	Sb ₂ O ₄ 0.03 Sb ₂ O ₃ 0.02	0.87	260.5	76.0	-0.8	1.0
4	Sb ₂ O ₄ 0.05	0.71	259.5	73.5	-0.6	1.3
比較例 1 f	Sb ₂ O ₃ 0.03	0.70	262.5	69.6	-0.9	0.8
2	Sb ₂ O ₃ 0.03	0.77	261.2	66.0	-0.9	1.1
3	Sb ₂ O ₃ 0.03 Sb ₂ O ₃ 0.02	0.92	262.3	59.5	-1.1	0.7

Key for Table 1:

a) Experiment No.; b) Catalyst mol%; c) Limiting viscosity; d) Softening point; e) Embodiment; f) Comparative Example.

Embodiment 2

222 mol% of ethylene glycol, 0.1 mol% of calcium acetate monohydrate as a catalyst, and 0.03 mol% of antimony tetroxide were added to dimethyl terephthalate to carry out the ester exchange reaction and the reaction temperature was gradually elevated to 277°C to carry out polymerization. After reacting under atmospheric pressure for 30 min., under a reduced pressure of 15 mmHg for 30 min. and under further reduced pressure of 0.1 mmHg to continue the reaction. At the point of 120 min. from the beginning of the reaction under a high vacuum state of 0.1 mmHg, the mixture was sampled and various measurement values were determined. The results are shown in Table 1.

Embodiment 3

222 mol% of ethylene glycol, 0.1 mol% of calcium acetate monohydrate as a catalyst, and 0.03 mol% of antimony tetroxide were added to dimethyl terephthalate to carry out the ester exchange reaction and the reaction was carried out under atmospheric pressure for 30 min., under a reduced pressure of 15 mmHg for 30 min. while the reaction temperature was gradually elevated to 277°C. At the point when the reaction was continued under 15 mmHg for 30 min., nitrogen gas was introduced to interrupt the vacuum state and 0.02 mol% of antimony trioxide was added. The pressure was reduced again and the reaction was carried out under a high vacuum state of 0.1 mmHg for 120 min. At this point, the reaction mixture was sampled and various values were measured. The results are shown in Table 1.

Embodiment 4

222 mol% of ethylene glycol and 0.1 mol% of calcium acetate monohydrate as a catalyst were added to dimethyl terephthalate to carry out the ester exchange reaction. A catalyst solution prepared by dissolving 0.05 mol% of antimony tetroxide in 30 mol% of ethylene glycol at 250°C under pressure was added and further 0.1 mol% of aqueous phosphoric acid solution was added to carry out the reaction. At the point after the reaction was carried out under atmospheric /164 pressure for 30 min., under a reduced pressure of 15 mmHg for 30 min. and under a further reduced pressure of 0.1 mmHg for 120 min., various values were determined and the results are shown in Table 1. As the amount of antimony tetroxide increased, the value L indicating color of the polyester tended to decrease.

Comparative Example 1

The reaction was carried out under the same reaction conditions and reaction operations as in Embodiment 1 except for using 0.03 mol% of antimony trioxide instead of 0.03 mol% of antimony tetraoxide. Various data are shown in Table 1.

Comparative Example 2

The reaction was carried out under the same reaction conditions and reaction operations as in Embodiment 2 except for using 0.03 mol% of antimony trioxide instead of 0.03 mol% of antimony tetroxide. Various data are shown in Table 1.

Comparative Example 3

Except that 0.03 mol% of antimony trioxide was added instead of 0.03 mol% of antimony tetroxide prior to the ester exchange reaction in Embodiment 3, the reaction was carried out as in Embodiment 3. Various data are shown in Table 1.

Comparative Example 4

[REDACTED]
[REDACTED]
[REDACTED] The reaction was carried out as in Embodiment 1. The polyester obtained had a limiting viscosity of 0.67, a softening point of 260°C, coloring L = 725, a = - 0.8 and b = 0.8.

Compared to Embodiment 1, the polyester obtained demonstrated a lower L value, which was not favorable.

Comparative Example 5

Except that 0.03 mol% of antimony pentoxide was used instead of antimony tetroxide as in Embodiment 1, the reaction was carried out as in Embodiment 1. The polyester obtained had a limiting viscosity of 0.65, a softening point of 258.9°C, coloring L = 75.0, a = - 0.8 and b = +2.0.

Cited References:

Japanese Patent No. Sho 39-6397

Chemical Dictionary 4 Term for diantimony tetroxide 9/30/1960, pp 277, Kyoritsu Shuppan.